

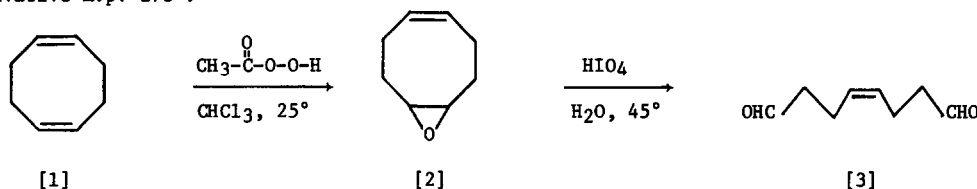
PERIODIC ACID CLEAVAGE OF EPOXIDES IN AQUEOUS MEDIUM

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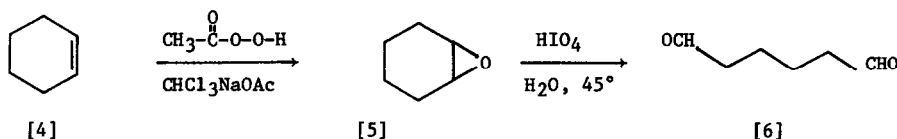
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It has been reported that imino ethers on oxidation with *m*-chloroperbenzoic acid (MCPBA) yield alkoxyoxaziranes which in acid medium cleaves to yield a carbonyl function and substituted hydroxylamine.<sup>1</sup> In connection with our work on peracids, we wish to report an efficient method for direct oxidation of epoxides to aldehydes with periodic acid in aqueous medium. The reaction of 10.8 g (0.1 mol) of 1,5-cyclooctadiene [1] with peroxyacetic acid,<sup>2</sup> 7.6 g (0.1 mol), in chloroform in the presence of 8.2 g (0.1 mol) sodium acetate, at room temperature, gives 5,6-epoxycyclooctene [2] in 80 % yield. bp. 52° (0.8 mm); nmr (neat),  $\delta$  5.5 (t, 2H), 2.85 (t, 2H), 1.9 (m, 8H). Oxidation of [2], 6.2 g (0.05 mol), with 9.6 g (0.05 mol) of periodic acid in water at 45° gives *cis*-4-octenedial<sup>3</sup> [3] in 76 % yield, bp. 61° (0.3 mm); nmr (neat),  $\delta$  9.83 (s, 2H), 5.6 (t, 2H), 2.10 (m, 8H); (Calc. for C<sub>8</sub>H<sub>12</sub>O<sub>2</sub>: C, 68.54; H, 8.56. Found: C, 68.41; H, 8.73 %). Reaction of [3] with 2,4-dinitrophenylhydrazine gives the 2,4-dinitrophenylhydrazone derivative m.p. 173°.



The reaction of cyclohexene [4], 16.4 g (0.2 mol), with peracetic acid, 15.2 g (0.2 mol), and sodium acetate, 16.4 g (0.2 mol), in chloroform at room temperature gives 1,6-epoxycyclohexane [5]. Epoxycyclohexane, 9.8 g (0.1 mol), on oxidation with periodic acid, 19.2 g (0.1 mol), in water at 45° gives 1,6 hexanedial, [6], in 82 % yield. bp. 49° (0.5 mm); nmr (neat),  $\delta$  9.6 (s, 2H), 1.8 (m, 8H). The 1,6-hexanedial was further characterized by conversion to the 2,4-dinitrophenylhydrazone. m.p. 168°.

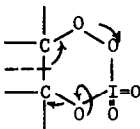


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The oxidation of 1,2-epoxyethylbenzene, 12.0 g (0.1 mol), with periodic acid, 19.2 g (0.1 mol), in water at 45° yields benzaldehyde in 70 % yield. bp. 178° (760 mm); nmr (neat),  $\delta$  9.25 (s, 1H), 7.1 (m, 2H), 6.75 (m, 3H). The benzaldehyde was further characterized by conversion to the 2,4-dinitrophenylhydrazone m.p. 236° (lit m.p. 237°).<sup>4</sup>

This procedure provides a method for the cleavage of epoxides in aqueous medium to give aldehydes in about 70 % yield. The above oxidation proceeds to yield the aldehydes even in the presence of unsaturation and is applicable to epoxides of sidechains substituted to aromatic systems. This unusual oxidation does not necessarily proceed by an intermediate glycol formed as a result of the cleavage of the epoxides in acid medium. This has been demonstrated after performing the above mentioned reactions in a buffered solution at pH 7.2. The major hurdle in the scheme is the polymerization of the aldehydes [3,6]. This can, however, be overcome by isolating the aldehyde at pH 7.0, following the periodic acid oxidation, and protecting the aldehyde by addition of a small crystal of hydroquinone during distillation.

A possible mechanism for the oxidation could be visualized as the formation of a periodate complex of the epoxide and subsequent cleavage as illustrated below.



Acknowledgement.

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#### References

- 1) D. Thomas and Donald H. Aue, *Tetrahedron Lett.*, 21, 1809 (1973).
- 2) M. Korach, Donald R. Nielsen, *J. Amer. Chem. Soc.*, 82, 4328 (1960).
- 3) In both 1,5-cyclooctadiene [1] and the monoepoxide [2] the double bond is cis. The mild oxidation of [2] with periodic acid does not change the cis configuration of the double bond in the product 4-octenedial [3].
- 4) A. Vogel, "Textbook of Practical Organic Chemistry," 3rd ed., John Wiley & Sons, Inc., New York, N.Y., 1966, p 723.